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⑤④ **Diarylide/disazo pyrazolone pigment compositions.**

⑤⑦ Diarylide pigments and disazopyrazolone pigments are provided which have improved properties achieved by incorporating certain azomethine compositions. The resultant pigments are useful in both water-based and solvent-based printing ink and coating compositions.

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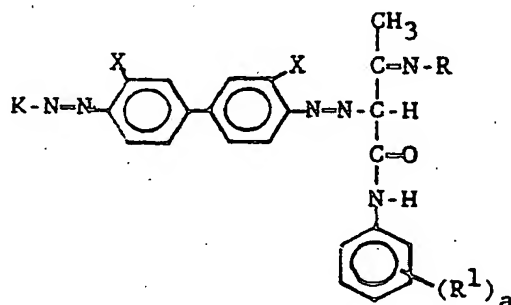
## DIARYLIDE/DISAZO PYRAZOLONE PIGMENT COMPOSITIONS

The present invention relates to improved diarylide and disazo pyrazolone pigments.

Diarylide and disazo pyrazolone pigments represent important types of general purpose colorants.

These types of pigments are well known in the prior art and are extensively used as colorants for solvent and water-based inks, coatings, paints and plastics. However, the diarylide and disazo pyrazolone pigments of the present invention exhibit higher coloring strength, clearer shades, lower rheology and enhanced gloss compared with prior art pigments.

The improved pigment compositions of the present invention are obtained by incorporating novel azomethine compounds in the pigment. These azomethines may be represented by the formula:



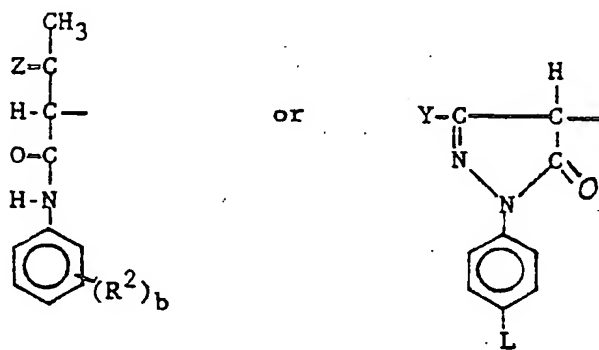
wherein:

R is an alkylene oxide polymer;

R<sup>1</sup> is independently selected from the group consisting of CH<sub>3</sub>, OCH<sub>3</sub>, OCH<sub>2</sub>CH<sub>3</sub> and Cl;

a is an integer of 0 to 5;

X is selected from the group consisting of Cl, CH<sub>3</sub> and K is:



wherein:

R<sup>2</sup> is independently selected from the group consisting of CH<sub>3</sub>, OCH<sub>3</sub>, OCH<sub>2</sub>CH<sub>3</sub> and Cl;

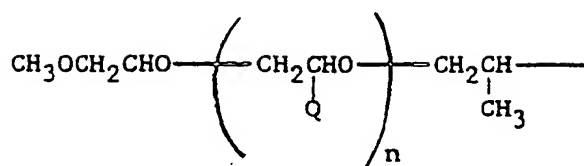
b is an integer of 0 to 5;

Z is selected from the group consisting of O and N-R;

Y is selected from the group consisting of CH<sub>3</sub> and COOC<sub>2</sub>H<sub>5</sub>; and

L is selected from the group consisting of CH<sub>3</sub> and H.

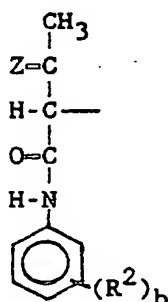
Preferably the alkylene oxide polymer (or oligomer) has a number average molecular weight of from about 500 to about 20,000 and the alkylene moiety contains 2 to 8 carbon atoms. Especially preferred are those in which the polymer has a number average molecular weight of 1,000 to 5,000. The preferred choice of the alkylene oxide polymer is ethylene oxide polymer, propylene oxide polymer and a copolymer of ethylene oxide and propylene oxide, such as those copolymers having the formula:



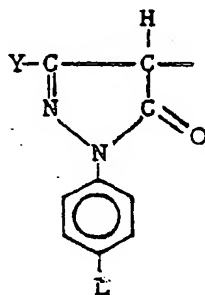
wherein:

n is an integer of about 4 to about 200, preferably 4 to 60; and Q is selected from the group consisting of H and  $\text{CH}_3$ .

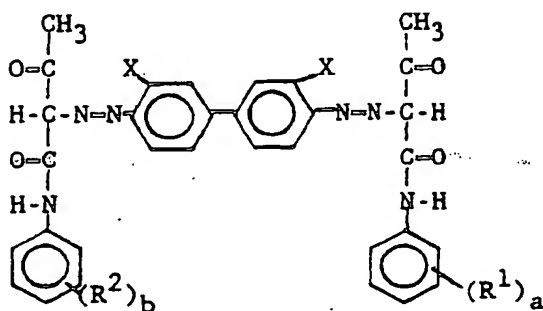
The azomethine will typically be present in the pigment composition in an amount of not more than about 50 wt. %, preferably 5 to 30 wt. %, based on the weight of the composition (i.e. pigment plus azomethine). In the case of a diarylide pigment, the azomethine is one wherein the moiety "K" has the value:



In the case of a disazo pyrazolone pigment, the azomethine is one wherein the moiety "K" has the value:

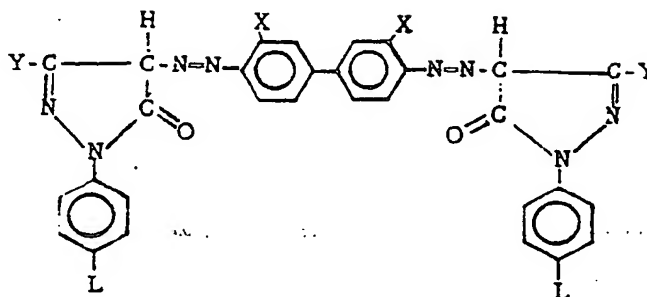


Typical diarylide pigments have the following general formula:



wherein X,  $\text{R}^1$ ,  $\text{R}^2$ , a and b have the values as set forth above.

Typical disazo pyrazolone pigments have the following general formula:



wherein X, Y and L have the values as set forth above.

Preferably, the diarylide pigment is one such as Pigment Yellow 12, Pigment Yellow 13, Pigment Yellow 14, Pigment Yellow 17, Pigment Yellow 83, Pigment Yellow 114, Pigment Yellow 116, Pigment Yellow 117, Pigment Yellow 176 and Pigment Orange 16. The disazo pyrazolone pigment is preferably one such as Pigment Orange 13, Pigment Orange 34, Pigment Red 37, Pigment Red 38, Pigment Red 41 and Pigment Red 41.

Printing inks are readily prepared from the pigment compositions of this invention by incorporating the desired aqueous and/or non-aqueous vehicle in the pigment plus azomethine in the usual manner. The typical surfactants, waxes, resins, extenders, etc. may also be incorporated as desired.

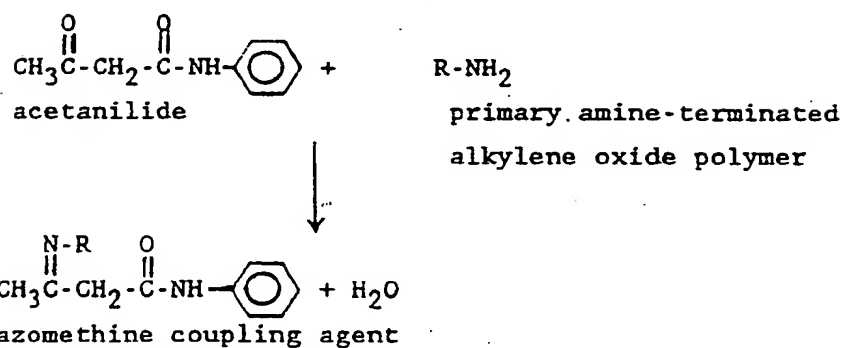
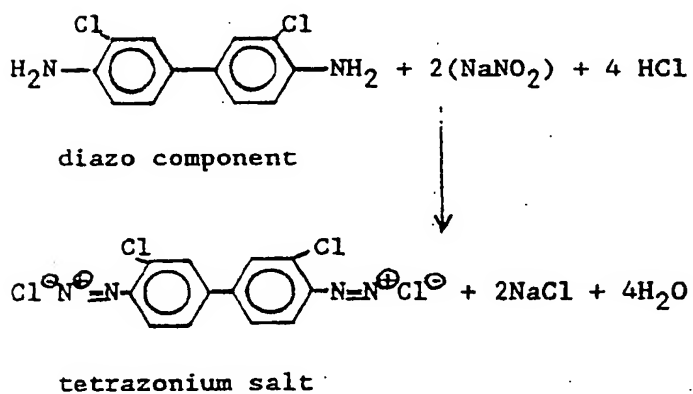
The novel azomethines of the present invention may be synthesized and subsequently added to the desired diarylide or disazo pyrazolone pigment. If this method is employed, the azomethine should be added as the pigment is being prepared. However, the preferable approach is one which involves the following steps:

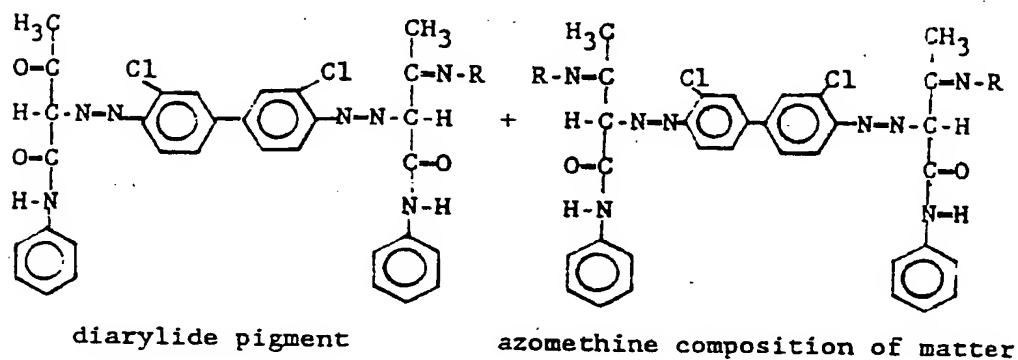
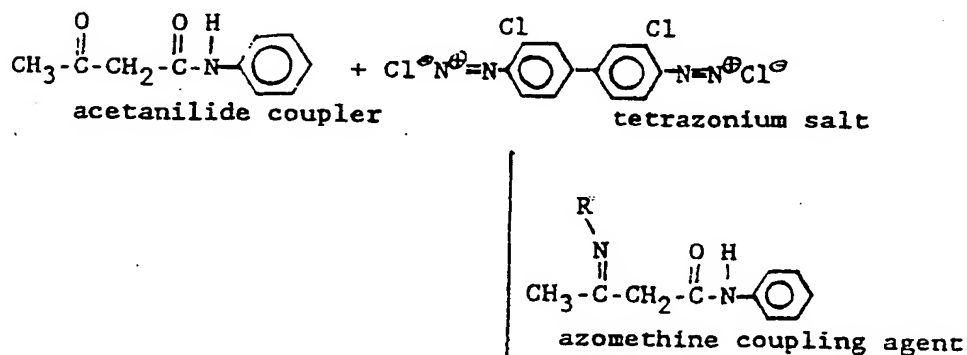
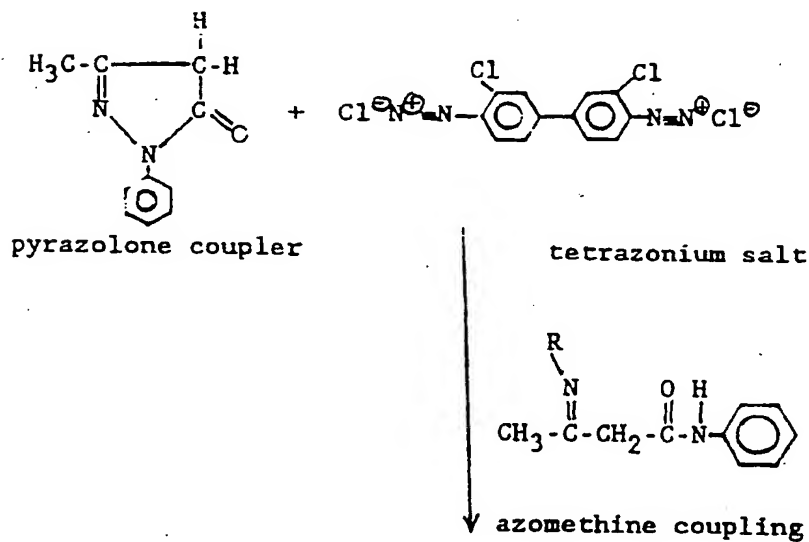
(a) formation of an azomethine coupling agent by reacting a primary amine-terminated alkylene oxide polymer and an acetanilide;

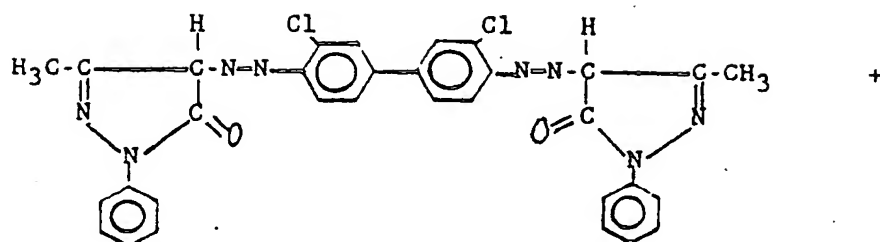
(b) formation of a tetrazonium salt by reaction of the desired diazo component with sodium nitrite and hydrochloric acid;

(c) reaction of the tetrazonium salt with the desired coupler in the presence of the azomethine coupling agent so as to produce the azomethine together with the pigment.

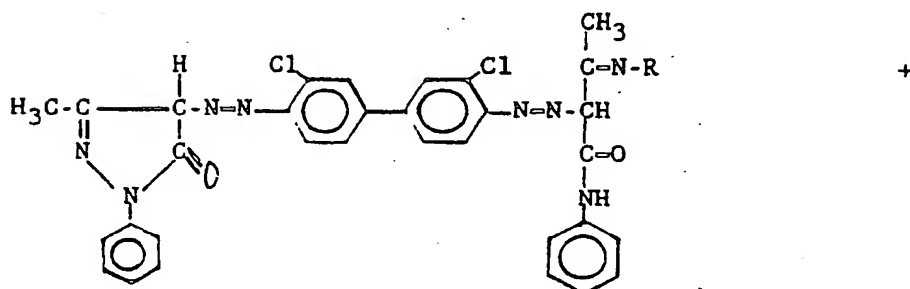
The following reactions generally illustrate the reaction scheme involved in steps (a) - (c):

(a) Azomethine Coupling Agent Formation(b) Tetrazonium Salt Formation

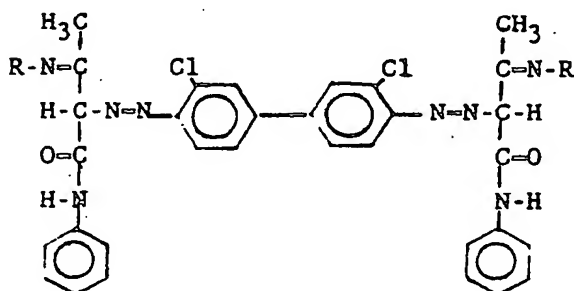
(c) Azomethine-Modified Diarylide Pigment Formation(c) Azomethine-Modified Disazo Pyrazolone Modified Pigment Formation



### Disazo-Pyrazolone Pigment



azomethine composition of matter



azomethine composition of matter

In the case of diarylide pigments, the tetrazonium salt is usually formed from 3,3'-dichlorobenzidine or dianisidine and the coupler is usually acetoacetanilide, substituted acetoacetanilides or mixtures of various acetoacetanilides. In a similar vein, for disazo pyrazolone pigments, the same type of tetrazonium salt is employed in conjunction with a pyrazolone, substituted pyrazolone or mixtures of various pyrazolones. The azomethine coupler is typically derived from an acetoacetanilide, such as acetoacetanilide, acetoacet-1,4-xylylene, acetoacet-o-toluidide, acetoacet-o-anisidine or acetoacet-2,5-dimethoxy-4-chloranilide.

The following examples illustrate the preparation of the novel azomethines and the azomethine-modified diarylide and disazo pyrazolone pigment compositions of the present invention.

### Example 1

Tetrazotized 3,3'-dichlorobenzidine (DCB) was prepared by charging 21.7 parts of 3,3'-dichlorobenzidine to 39.8 parts of 20% Be HCl and 140 parts of an ice/water mixture with constant stirring to form a homogenous suspension. To this was then added 32.6 parts of 38% sodium nitrite and stirring continued for 1 hour at a temperature of 0 - 5°C. The excess nitrous acid was then destroyed by the addition of

approximately 0.5 parts sulfamic acid.

A fine suspension of acetoacetanilide (AAA) was prepared by charging 31.7 parts AAA to 400 parts H<sub>2</sub>O and 33.6 parts of 50% aqueous NaOH, and the mixture was stirred until all of the AAA was dissolved. The temperature of the solution was adjusted to 0 - 5° C. with the addition of ice and subsequently the AAA was precipitated by the slow addition of 38.5 parts of 70% acetic acid.

An azomethine coupling component was formed by charging 1.2 parts of AAA to 13.5 parts of a primary amine-terminated polymer comprised of 70% ethylene oxide and 30% propylene oxide and having a number average molecular weight of 2000 ("Jeffamine M-2070," Texaco Chemical Corp.) and heating the mixture to 100 - 105° C. with stirring. After 1 hour, the reaction was complete as evidenced by the disappearance of the ketone absorption band in the SR spectrum (approximately 1673 cm<sup>-1</sup>). The resulting azomethine was added to the suspension of AAA immediately prior to coupling with the tetrazotized DCB.

Coupling was then carried out by adding the tetrazotized DCB to the AAA suspension over a period of 1 hour. Stirring was continued until no excess tetrazo remained, and then the slurry was heated to 90 - 95° C., stirred 15 minutes, filtered, washed and dried in an oven at 60° C.

Evaluation was performed by charging 15 parts of the pigment to 75 parts of a water-based ink vehicle containing a commercial grade acrylic resin ("Joncryl 67", S.C. Johnson) and 300 parts of 1/8th inch stainless steel balls. The mixture was placed on a "Red Devil" paint shaker for 30 minutes, to produce a mill base. The viscosity of the mill base was approximately one-half of that of a conventional Pigment Yellow 11 mill base. Water flexo inks were prepared by letting back the mill bases with additional vehicle to a pigment content of 9.0%. The pigment produced an ink that was approximately 20% stronger, glossier and more transparent than those prepared from the conventional Pigment Yellow 12.

#### Example 2

Example 1 was repeated except that 32.7 parts of acetoacet-o-toluidide (AAOT) was used in place of the AAA. The resulting Pigment Yellow 14 when evaluated as in Example 1, gave similar results versus a conventional Pigment Yellow 14.

#### Example 3

The procedure of Example 2 was followed except the suspension of precipitated AAA and the azomethine coupler were added to the solution of tetrazo. Results were similar to those of Example 1.

#### Example 4

The procedure of Example 1 was followed except the product was converted to a 50% solids presscake, and evaluated by utilizing a shot mill in place of the paint shaker, to disperse the pigment. The resulting ink showed increased gloss, strength, and transparency compared with a conventional Pigment Yellow 14.

#### Example 5

Tetrazotized DCB, a fine suspension of AAA and an azomethine coupling component were obtained by the procedure of Example 1. Coupling was then carried out by simultaneously and separately adding the tetrazotized DCB and azomethine coupling component to the AAA suspension over a period of 1 hour. Stirring was continued until no excess tetrazo remained, and the slurry was then heated to 90 - 95° C., stirred for 15 minutes, filtered, washed and dried in an oven at 60° C.

Evaluation was performed by charging 15 parts of the pigment preparation to 75 parts of a publication gravure ink vehicle containing Zn/Ca resinate, toluene, and lecithin, and 150 parts of 1/8th inch stainless steel balls. The mixture was placed on a "Red Devil" paint shaker for 30 minutes to produce a mill base. A



finished ink was obtained by diluting the mill base with additional vehicle to a standard viscosity (30 seconds through a #1 Zahn Cup). The pigment preparation produced an ink that was 30% stronger, glossier, and more transparent than an untreated pigment. The pigment preparation was lower in mill base viscosity and greener in color evaluation versus conventional amine treated Yellow 12.

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#### Example 6

10 The procedure of Example 1 was followed except using 20.9 parts of o-dianisidine in place of the 21.7 parts of 3,3'-dichlorobenzidine to afford 62.2 parts of Pigment Orange 16.

Evaluation was performed in a C-Type packaging gravure ink by charging 15 parts of pigment to 75 parts of a RS-nitrocellulose based grind vehicle with 300 parts of 1/8th inch stainless steel balls. The mixture was placed on a "Red Devil" paint shaker for 30 minutes to afford a mill base, which was then  
15 further letdown with 180 parts of a typical maleic resin solution containing toluene and isopropyl alcohol. The ink was then adjusted to print viscosity (22 seconds through a #2 Zahn cup) by the addition of isopropyl acetate. Compared with an ink made from conventionally prepared Orange 16, the ink of this invention was 30% stronger, glossier, more transparent, and lower in rheology. To demonstrate the versatility of the invention, these pigments were also evaluated in a water-based flexographic ink according  
20 to the method in Example 1. The Orange 16 of this invention was again stronger, glossier and more transparent than the untreated Orange 16.

#### Example 7

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The procedure of Example 1 was followed except using 46.5 parts of acetoacet-2,5-dimethoxy-4-chloro aniline in place of the 31.7 parts of acetoacetanilide, to afford 82.1 parts of Pigment Yellow 83. The resulting material was evaluated as in Example 6, versus an untreated Yellow 83; the former was considerably  
30 stronger, glossier and more transparent in both the solvent-based and water-based inks.

#### Example 8

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The procedure of Example 1 was followed except using 15.8 parts of acetoacetanilide and 17.0 parts of acetoacet-p-toluidide in place of the 31.7 parts of acetoacetanilide to afford 64.5 grams of Pigment Yellow 114. Versus an untreated sample of Pigment Yellow 114, the pigment preparation of the example showed enhanced gloss, strength, transparency and rheology in both water-based and solvent-based flexographic  
40 inks.

As can be seen by the above Examples 1 - 8, the modified diarylide pigments achieved significantly improved properties. Specifically, the modified diarylide pigments are characterized by a lower viscosity, in addition to improved strength, gloss and transparency.

The modified diarylide pigments may be used in all applications where diarylide pigments are utilized.  
45 They are especially useful in water-based flexographic inks, water-based gravure inks, water-based news inks and any water-based coatings where diarylide pigments are utilized. They are also useful in solvent-based inks, including solvent-flexographic inks, publication gravure inks, various solvent packaging inks, and solvent-based coatings where diarylide pigments are utilized.

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#### Example 9

Tetrazotized 3,3'-dichlorobenzidine (DCB) was prepared by charging 17.5 parts of DCB to 100 parts of an ice/water mixture and 32.1 parts of 20% Be HCl, with constant stirring, to form a homogenous  
55 suspension. To this was then added 35.7 parts of a 28% aqueous solution of sodium nitrite and stirring continued for 1 hour at a temperature of 0 - 5° C. After one hour, excess nitrous acid was destroyed with the addition of approximately 0.5 parts of sulfamic acid.

A fine suspension of 1-phenyl-3-methyl-5-pyrazolone (PMP) was prepared by charging 25.2 parts of PMP to 400 parts of H<sub>2</sub>O and 13.1 parts of 50% aqueous sodium hydroxide, and the mixture was stirred until all the PMP was dissolved. The PMP was then precipitated by the slow addition of 15 parts of 70% acetic acid.

5 An azomethine coupling component (1) was formed by charging 0.7 parts of acetoacetanilide (AAA) to 7.9 parts of the same amine-terminated polymer as employed in Example 1, and heating the mixture to 100 - 105 °C. while stirring. After one hour, the reaction was complete as evidenced by the disappearance of the ketone absorption band in the IR spectrum at 1673 cm<sup>-1</sup>.

10 Formation of the Orange 13 pigment composition of the invention was then achieved by the simultaneous addition of the tetrazotized DCB and the azomethine compound (1) to the PMP suspension over a period of 70 minutes. Stirring was continued until no excess tetrazotized DCB remained, and then the slurry was heated to 90 - 95 °C., stirred an additional 15 minutes, filtered, washed, and dried in an oven at 60 °C., to give 51.0 parts of an Orange 13 pigment composition.

15 Evaluation was performed by charging 15 parts of the pigment to 75 parts of a water-based ink vehicle containing a commercial grade acrylic resin ("Joncyl 67", S.C. Johnson) and 300 parts of 1/8th inch stainless steel balls. The mixture was placed on a "Red Devil" paint shaker for 30 minutes, to produce a mill base. The viscosity of the mill base was approximately one-half of that of a conventional Pigment Orange 13 mill base. Water flexo inks were prepared by letting back the mill bases with additional vehicle to a pigment content of 9.0%. The pigment produced an ink that was approximately 30% stronger, glossier and more transparent than those prepared from the conventional Pigment Orange 13.

20 To demonstrate the versatility of the invention, evaluation was also performed in a C-type packaging gravure ink by charging 25 parts of pigment to 75 parts of a RS-nitrocellulose-based grind vehicle with 300 parts of 1/8th inch stainless steel balls. The mixture was placed on a "Red Devil" paint shaker for 30 minutes to afford a mill base, which was then further letdown with 180 parts of a typical maleic resin solution containing toluene and isopropyl alcohol. The ink was then adjusted to print viscosity (22 seconds through a #2 Zahn cup) by the addition of isopropyl acetate. Compared with an ink made from conventionally prepared Orange 13, the ink of this invention was 30% stronger, glossier, more transparent, and lower in rheology.

#### 30 Example 10

The procedure of Example 9 was repeated except using 26.5 parts of 1-(p-tolyl)-3-methyl-5-pyrazolone in place of the 25.2 parts of 1-phenyl-3-methyl-5-pyrazolone, to afford 53.0 parts of an Orange 34 pigment composition.

Evaluation of this pigment composition in both the water flexo and C-type packaging gravure ink systems of Example 9 gave similar improvements over a conventional Orange 34 made without the azomethines of this invention.

#### 40 Example 11

45 Tetrazotized o-dianisidine (ODA) was prepared by charging 19.5 parts of ODA to 100 parts of an ice/water mixture and 37.1 parts of 200 Be HCl, with constant stirring to form a homogenous suspension. To this was added 12.1 parts of sodium nitrite and stirring was continued for 90 minutes at a temperature of 0 - 5 °C. Remaining nitrous acid was eliminated with the addition of approximately 0.5 parts of sulfamic acid.

50 A fine suspension of 1-(p-tolyl)-3-methyl-5-pyrazolone (PTMP) was prepared according to the procedure of Example 1 using 30.8 parts of PTMP, 600 parts of water, 15.0 parts of 50% aqueous sodium hydroxide, and 17.0 parts of 70% acetic acid.

55 Formation of an improved pigment Red 37 was then achieved by the simultaneous addition of the tetrazotized ODA and 9.4 parts of azomethine compound (1) to the PTMP suspension over a period of 70 minutes, while maintaining a pH of 5.1 - 5.6 by the addition of dilute aqueous sodium hydroxide. Stirring was continued until no excess tetrazotized ODA remained, and then the slurry was heated to 90 - 95 °C., stirred an additional five minutes, cooled to 70 °C., filtered, washed with water, and dried in an oven at 60 °C. to give 61 parts of a Pigment Red 37 composition.

Evaluation of this pigment composition in both the water flexo and C-type packaging gravure ink

systems of Example 9 gave similar improvements over a Pigment Red 37 prepared without the azomethine compound of this invention.

#### Example 12

The procedure of Example 11 was repeated except using 28.4 parts of 1-phenyl-3-methyl-5-pyrazolone (PMP) in place of the 1-(p-tolyl)-3-methyl-5-pyrazolone (PTMP) to afford 58.0 parts of a similarly improved Pigment Red 41.

#### Example 13

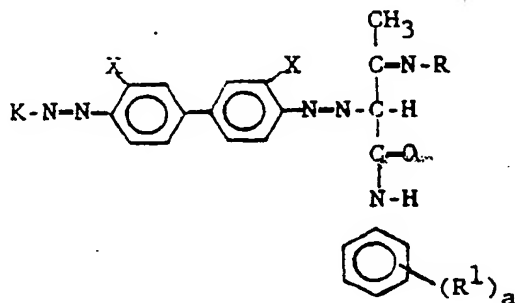
The procedure of Example 9 was repeated except using an azomethine coupling component made from 7 parts acetoacetanilide and 7.9 parts of a primary amine-terminated polymer comprised of 95% propylene oxide and 5% ethylene oxide and having a number average molecular weight of 2000 ("Jeffamine M 2005," Texaco Chemical Corporation), to give 51.0 parts of an Orange 13 pigment composition having increased gloss and transparency in C-type gravure packaging ink, compared with the Orange 13 of Example 9.

#### Example 14

The procedure of Example 13 was repeated except that 12.0 parts of Rosin were added to the pigment slurry at 90 - 95°C., prior to filtration. The resulting Pigment Orange 13 composition showed greatly enhanced strength and dispersability for the coloration of polyvinyl-chloride (PVC).

#### Claims

1. An azomethine compound having the formula:



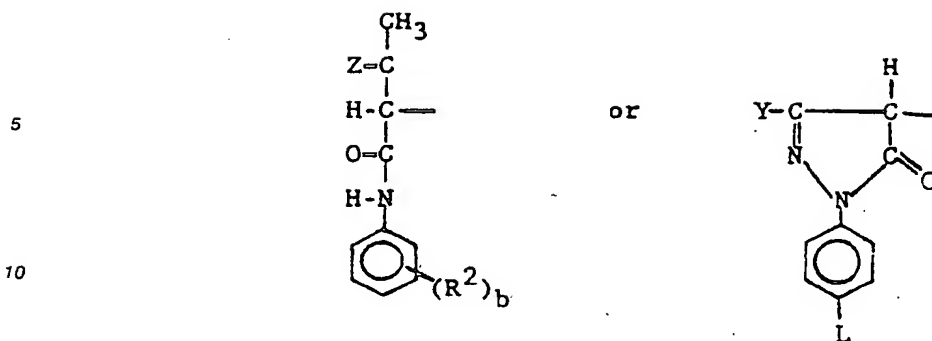
wherein:

R is an alkylene oxide polymer;

R<sup>1</sup> is independently selected from the group consisting of CH<sub>3</sub>, OCH<sub>3</sub>, OCH<sub>2</sub>CH<sub>3</sub> and Cl;

a is an integer of 0 to 5;

X is selected from the group consisting of Cl, CH<sub>3</sub> and K is:



15 wherein:

$R^2$  is independently selected from the group consisting of  $CH_3$ ,  $OCH_3$ ,  $OCH_2CH_3$  and  $Cl$ ;

$b$  is an integer of 0 to 5;

$Z$  is selected from the group consisting of  $O$  and  $N-R$ ;

$Y$  is selected from the group consisting of  $CH_3$  and  $COOC_2H_5$ ; and

20  $L$  is selected from the group consisting of  $CH_3$  and  $H$ .

2. The azomethine compound of claim 1, wherein the alkylene oxide polymer has a number average molecular weight of from about 500 to about 20,000 and the alkylene moiety contains 2 to 8 carbon atoms.

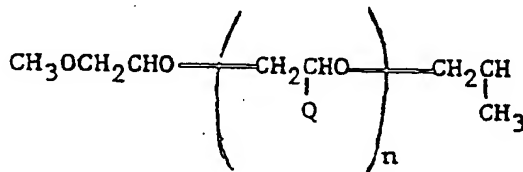
3. The azomethine compound of claim 2, wherein the polymer has a number average molecular weight of 1,000 to 5,000.

25 4. The azomethine compound of claim 2, wherein the alkylene oxide polymer is an ethylene oxide polymer.

5. The azomethine compound of claim 2, wherein the alkylene oxide polymer is a propylene oxide polymer.

6. The azomethine compound of claim 2, wherein the alkylene oxide polymer is a copolymer of ethylene oxide and propylene oxide.

30 7. The azomethine compound of claim 6, wherein the copolymer has the formula:



40 wherein:

$n$  is an integer of about 4 to about 200, and  $Q$  is selected from the group consisting of  $H$  and  $CH_3$ .

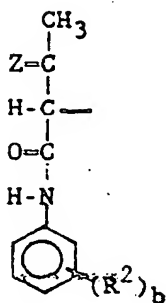
8. The azomethine compound of claim 7, wherein  $n$  is 4 to 60.

9. A pigment composition comprising an azomethine compound of any one of claims 1 to 8 and at least one pigment.

45 10. The pigment composition of claim 9, wherein the azomethine is present in an amount of not more than about 50 wt.

11. The pigment composition of claim 10 wherein the azomethine is present in an amount of 5 to 30 wt. %.

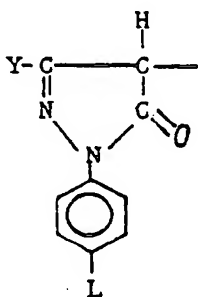
50 12. A pigment composition comprising at least one diarylide pigment and an azomethine compound of any one of claims 1 to 8 wherein  $K$  is:



13. The pigment composition of claim 12 wherein the diarylide pigment is selected from the group consisting of Pigment Yellow 12, Pigment Yellow 13, Pigment Yellow 14, Pigment Yellow 17, Pigment Yellow 83, Pigment Yellow 114, Pigment Yellow 126, Pigment Yellow 127, Pigment 176 and Pigment Orange 16.

14. A printing ink composition comprising the pigment composition of claim 12 and a vehicle.

15. A pigment composition comprising at least one disazopyrazolone pigment, and an azomethine compound of any one of claims 1 to 8 wherein K is:



16. The pigment composition of claim 15 wherein the disazopyrazolone pigment is selected from the group consisting of Pigment Orange 13, Pigment Orange 34, Pigment 37, Pigment Red 38, Pigment Red 41 and Pigment Red 42.

17. A printing ink composition comprising the pigment composition of claim 15 and a vehicle.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 90109686.7
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
A	<u>US - A - 3 776 749</u> (MC KAY et al.) * Claims 1,5,9 *	1,9, 12,15	C 09 B 35/08 C 09 B 67/22 C 09 D 11/02
A	<u>DE - A - 2 204 769</u> (BAYER AG) * Claims *	1,9, 12,14, 15,17	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
			C 09 B C 09 D
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 28-08-1990	Examiner HAUSWIRTH
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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